



## CoO and g-C<sub>3</sub>N<sub>4</sub> complement each other for highly efficient overall water splitting under visible light

Feng Guo<sup>a,b</sup>, Weilong Shi<sup>a,c</sup>, Cheng Zhu<sup>a</sup>, Hao Li<sup>a</sup>, Zhenhui Kang<sup>a,\*</sup>

<sup>a</sup> Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 199 Ren'ai Road, Suzhou, 215123, Jiangsu, PR China

<sup>b</sup> Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region, Ministry of Education, School of Environmental Science and Engineering, Chang'an University, Xi'an, 710064, PR China

<sup>c</sup> School of Physics, Huazhong University of Science and Technology, Wuhan, 430074, PR China



### ARTICLE INFO

#### Keywords:

CoO nanoparticles  
g-C<sub>3</sub>N<sub>4</sub>  
Photothermal deactivation  
H<sub>2</sub>O<sub>2</sub>-resistence poisoning  
Overall water splitting

### ABSTRACT

Photocatalytic hydrogen production from overall water splitting is a clean and renewable technology that can convert solar energy into chemical energy, for which developing an efficient and stable photocatalyst has been the central scientific topic. Herein, CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalysts were fabricated through a facile solvothermal method for overall water splitting. Simultaneous evolution of H<sub>2</sub> and O<sub>2</sub> from pure water with the stoichiometric ratio of about 2:1 achieved with all the CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions as catalysts under visible light irradiation. Among of them, 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> with H<sub>2</sub> evolution rate of 2.51 μmol/h and O<sub>2</sub> evolution rate of 1.39 μmol/h also exhibited remarkably higher photocatalytic performance and stability (over 15 cycles) than single CoO or g-C<sub>3</sub>N<sub>4</sub>. This enhanced photocatalytic activity of CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction can be ascribed to the synergistic effect of junction and interface formed between CoO and g-C<sub>3</sub>N<sub>4</sub>. In addition, the sufficient long lifetime stability of CoO/g-C<sub>3</sub>N<sub>4</sub> comes from the complementary advantages effect between CoO and g-C<sub>3</sub>N<sub>4</sub>, as is proved, CoO can protect g-C<sub>3</sub>N<sub>4</sub> from H<sub>2</sub>O<sub>2</sub> poisoning, and simultaneously the photo-induced heat from CoO during the photocatalytic process responsible for the rapid deactivation can be timely conducted to g-C<sub>3</sub>N<sub>4</sub>.

### 1. Introduction

As a potential means of renewable energy production, photocatalytic water splitting under visible light has been considered as an advanced edge study in the current photocatalysis [1,2]. Since the pioneering work of Fujishima and Honda in 1972 [3], numerous semiconductor materials, such as metal oxides [4,5], nitrides [6], and sulfides [7], have been extensively studied for producing hydrogen from water. Nevertheless, most of developed single-component photocatalysts still suffer from kinds of limits, such as wide band gaps, instability and the rapid recombination of electron-hole pairs, etc [8,9]. In this case, enormous efforts have been made in tuning the semiconductor's interface and surface engineering. Sparked by the natural photosynthetic systems found in plant leaves, Z-scheme photocatalytic system consisting of two different photocatalysts is one of the most promising strategies to achieve water splitting [10]. In this concept, the water-splitting system can be separated into two parts: the photo-generated electrons in the higher conduction band for H<sub>2</sub> evolution and holes in the lower valence band (VB) for O<sub>2</sub> evolution, such as

MgTa<sub>2</sub>O<sub>6-x</sub>N<sub>y</sub>/TaON [11], SrTiO<sub>3</sub>:Rh/BiVO<sub>4</sub> [12], and RuO<sub>2</sub>-TaON/Pt-TaON [13]. Another potential strategy to split water is loading cocatalysts (e.g. Pt [14], Ru [15], Rh [16] and transition metals [17]) on the surface of a semiconductor to promote its photocatalytic activity. In the view of this system, the metal cocatalyst acts like an electron trap to effectively separate the photogenerated charges, and suppress the back reaction of water formation from evolved H<sub>2</sub> and O<sub>2</sub>. Apart from the above two systems, recent years have witnessed a flourish of interest in engineering heterojunctions in photocatalysts to split water under visible light irradiation. In the heterostructured system, heterojunction photocatalysts can not only extend visible-light response, but also promote efficiently spatial separation of the electron-hole pairs. For example, many heterojunction photocatalysts (e.g. CdS/TiO<sub>2</sub> [18], CuO/TiO<sub>2</sub> [19] and Bi<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub> [20], etc) have been reported for photocatalytic H<sub>2</sub> generation under visible light irradiation owing to the perfect band alignment and the highly efficient electron transfer. Although the construction of heterojunction photocatalysts provides a meritorious platform in the photocatalysis, recent engineering the heterojunction photocatalysts has mainly focused on how to effectively

\* Corresponding author.

E-mail address: [zhkang@suda.edu.cn](mailto:zhkang@suda.edu.cn) (Z. Kang).

separate the electron-hole pairs based on the band structures of the semiconductors. Conversely, less emphasis is placed on the selection of semiconductors before engineering the heterojunction photocatalysts. In fact, it is very significant and should not be neglected besides the band energy alignments because every kind of semiconductors has its merits and demerits. In order to perfect the fabrication of heterojunction photocatalysts, it is significant to design a heterojunction photocatalyst not only possessing band energy alignments but also meeting complementary advantages of two photocatalysts for water splitting. As an example, we preliminary designed a CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst to explain our idea.

Recent years, cobalt monoxide (CoO) photocatalyst has gained more attention since Bao et al. reported CoO exhibited overall water splitting with an extraordinary STH of around 5% in 2014 [21]. However, the fatal defect for CoO is severely deactivated, thus impeding its further practical application. Undoubtedly, solving the CoO deactivation has been of great importance in the photocatalysis [21,22]. So far, two main reasons leading to CoO deactivation have been reported, one of which corresponds to CoO nanoparticles aggregation, the other reason originates from the unintended thermo-induced oxidation of CoO during photocatalytic process [23]. Also, it should be particularly noted that we found that CoO photocatalyst possesses outstanding anti-H<sub>2</sub>O<sub>2</sub> poisoning ability, which provides a new perspective in the design of H<sub>2</sub>O<sub>2</sub>-resistance composite photocatalysts to avoid many single-component photocatalysts poisoned by H<sub>2</sub>O<sub>2</sub> [23]. Considering the reasons of CoO deactivation and its advantages, it stimulates us to make a new attempt to search for a semiconductor combined with CoO to form the heterojunction photocatalyst, which not only solves the deactivation of CoO but also takes advantage of CoO superiority. And the suitable semiconductor photocatalyst in this system should be equipped with favorable thermal conductivity for heat dispersion, larger specific surface area keeping nanoparticles from aggregation and suitable band gap against the recombination of electron-hole pairs.

Fortunately, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) with its unique thermal, electrical and optical properties and moderate band gap of around 2.7 eV has been extensively applied in the field of photocatalysis [24,25]. Particularly, g-C<sub>3</sub>N<sub>4</sub> that consists exclusively of covalently-linked, sp<sup>2</sup>-hybridized carbon and nitrogen atoms not only possesses excellent thermal conductivity [26,27], but also could provide a large scaffold for anchoring various substrates to effectively prevent the aggregation of nanoparticles because of its large specific surface area and flexible 2D structure [28]. Nevertheless, apart from the main drawback of rapid recombination rate of electron-hole pairs, another fatal weakness of g-C<sub>3</sub>N<sub>4</sub> can be attributed that it is easily subject to being seriously poisoned by the generating H<sub>2</sub>O<sub>2</sub> during the photocatalysis, ultimately causing rapid inactivation [29,30]. Therefore, it is natural to conceive that coupling g-C<sub>3</sub>N<sub>4</sub> with CoO to form a long-term stable and high-effective heterojunction photocatalyst by mutually compensating the respective deficiency.

In this work, we report that CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst synthesized by one-step solvothermal method showed excellent photocatalytic activity for overall pure-water splitting. To clarify the effects of CoO content, both pristine CoO and g-C<sub>3</sub>N<sub>4</sub> were also investigated. The results demonstrate that all the CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions exhibit much higher photocatalytic performance and outstanding stability compared to individual CoO and g-C<sub>3</sub>N<sub>4</sub>. And the highest photocatalytic activity was obtained when the CoO content reaches 30 wt.% in the composite, which exhibited H<sub>2</sub> evolution rate of 2.51 μmol/h and O<sub>2</sub> evolution rate of 1.39 μmol/h. Meanwhile, 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> also displays the excellent durable photocatalytic stability (over 15 cycles). The enhanced photocatalytic activity of CoO/g-C<sub>3</sub>N<sub>4</sub> photocatalyst can be predominantly resulted from the formed heterostructure between CoO and g-C<sub>3</sub>N<sub>4</sub>, which contributes to the efficient separation of photo-generated electrons and holes. The excellent durable photocatalytic stability of CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction drives from the thermal conductivity of g-C<sub>3</sub>N<sub>4</sub> and outstanding H<sub>2</sub>O<sub>2</sub>-resistance

property of CoO [23]. Additionally, g-C<sub>3</sub>N<sub>4</sub> with large specific surface area and flexible 2D structure can effectively prevent CoO deactivation owing to the CoO nanoparticles aggregation.

## 2. Experimental section

### 2.1. Synthesis of CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions

The g-C<sub>3</sub>N<sub>4</sub> powders were prepared through annealing urea in muffle according to our previous report [30]. Typically, 10 g of urea was put in an alumina crucible with a cover under ambient pressure in air, heated to 550 °C for 3 h with a ramping rate of 0.5 °C/min to complete the reaction. CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions with different mass ratios of CoO (10 wt.%, 20 wt.%, 30 wt.%, 40 wt.% and 50 wt.%) were synthesized using the following procedure: different mass ratios of Co (CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.37, 0.83, 1.43, 2.22 and 3.33 g) and (1 g) g-C<sub>3</sub>N<sub>4</sub> powders were added to a mixed solvent containing 16 mL n-octanol and 64 mL ethanol by stirring for 2 h. The resulted slurry was transferred to a 100 mL Teflon-lined stainless steel autoclave, and then heated at 220 °C for 4 h. When the autoclave was cooled down to room temperature, the formed powders were washed with ethanol for three times and finally dried at 70 °C in the oven. The CoO nanoparticles were fabricated under the same conditions in the absence of g-C<sub>3</sub>N<sub>4</sub> powders.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using an X'Pert-ProMPD (olland) D/max- $\gamma$ A X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154178$  nm). Transmission electron microscope (TEM), high-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed with a FEI-Tecnai F20 microscope operating at 200 kV, respectively. Scanning electron microscopy (SEM) images were obtained with a FEI-quanta 200 microscope with an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatized Al K $\alpha$  X-ray source. Room temperature UV-vis absorption spectra were recorded on a Lambda 750 (Perkin Elmer) spectrophotometer in the wavelength range of 250–800 nm. Ultraviolet photoelectron spectroscopy (UPS) measurements were finished using an unfiltered He I (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. The Brunauer-Emmett-Teller (BET) specific surface areas and pore structures were characterized by a Micromeritics ASAP-2050 porosimeter. Photoluminescence (PL) study was recorded on a Fluorolog-TCSPC Luminescence Spectrometer. Electrochemical analysis was conducted on a CHI 660b workstation. The Pt wire, a calomel electrode, and the samples were served as the counter electrode, the reference electrode, and the working electrode in a three-electrode cell. Electrochemical impedance spectroscopy (EIS) was recorded by using an alternating voltage of 5 mV amplitude in the frequency range of 10<sup>5</sup> Hz to 10<sup>-2</sup> Hz with the open circuit voltage in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. For photocurrent versus time analysis and linear sweep voltammetry (LSV) curves, the Xenon lamp (100 mW cm<sup>-2</sup>) and Na<sub>2</sub>SO<sub>4</sub> (0.1 M) were employed as light source and electrolyte, respectively.

### 2.3. Photocatalytic activity measurement

For photocatalytic reactions, 50 mg of photocatalyst, 20 mL of ultrapure water and a stir bar were put into a photoreactor vial with a total volume of 50 mL. Afterwards, the system was degassed to completely remove air. Under constant stirring, a white light-emitting diode (LED) was applied as the visible light source ( $\lambda > 400$  nm). An online GC-7900 gas chromatograph (GC) set up with a thermal conductivity detector (TCD) and 5 Å molecular sieve columns was employed for the evolved gas detection. The temperatures of the oven, injection port and

detector in GC were held at 80, 100, and 120 °C, respectively. Ar was used as the carrier gas with a flow rate of 30 mL/min. For reproducibility and stability tests of the photocatalysts, the suspension after reaction was centrifuged and reused for repeated tests. The apparent quantum efficiency was estimated under a 300 W xenon lamp equipped with band pass filter (see the Supporting Information for details).

#### 2.4. Heat-treatment of photocatalysts

In a typical synthesis run, 50 mg of the as-prepared photocatalysts were dispersed in 20 mL ultrapure water with further transfer into a 50 mL vial (the same one for photocatalytic reaction). Then, the suspension was treated by heating for 6 h under various temperatures (40, 50, 60, 70 and 80 °C) under air atmospheres.

#### 2.5. Hydrogen peroxide ( $H_2O_2$ ) generation test

Formation of  $H_2O_2$  in the photocatalytic reaction system was detected by UV-vis spectroscopy using o-tolidine as the  $H_2O_2$  indicator. 2 mL of the reaction supernatant was collected after centrifugation, and then 0.5 mL of 1% o-tolidine in 0.1 M HCl solution was added into it. After about 2 min, the dispersion was further acidified with 2 mL of 1 M HCl, if there is  $H_2O_2$  existed in the solution, the color will change from transparent to yellow. Concentration of  $H_2O_2$  was then obtained by measuring the absorbance of the yellow product at a characteristic peak wavelength of 436 nm.

### 3. Results and discussion

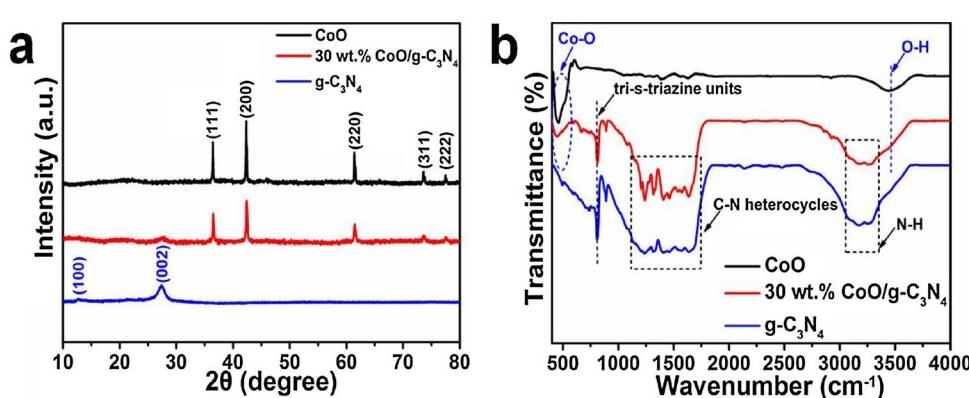
**Fig. 1a** shows the XRD patterns of g-C<sub>3</sub>N<sub>4</sub>, CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>. For g-C<sub>3</sub>N<sub>4</sub> (blue trace), two pronounced peaks at 13.1° and 27.3° are found, which are in good agreement with graphitic phase carbon nitride [31]. The lower angle diffraction peak at 13.1° corresponds to tri-s-triazine units (100), and the other stronger one at 27.3° is derived from the interlayer stacking of aromatic segments (002). For CoO (black trace), all the diffraction peaks can perfectly match with the face-centered cubic CoO structure (JCPDS 71-1178) [32]. In the case of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> (red trace), all the diffraction peaks of both g-C<sub>3</sub>N<sub>4</sub> and CoO can be observed in the XRD pattern. Furthermore, Fig. S1 displays the XRD patterns of all the as-prepared samples, indicating that with the increase of CoO concentration, the diffraction peaks intensity of CoO are more and more obvious, but two peaks belonging to g-C<sub>3</sub>N<sub>4</sub> get weaker. In addition, composition and structure of g-C<sub>3</sub>N<sub>4</sub>, CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> were further confirmed by FT-IR spectra (**Fig. 1b**). In the FT-IR spectrum of g-C<sub>3</sub>N<sub>4</sub>, the peak at near 808 cm<sup>-1</sup> is attributed to the characteristic breathing mode of tri-s-triazine units, and the peaks from 1200 to 1640 cm<sup>-1</sup> correspond to the typical stretching vibration modes of CN heterocycles. Another broad peak at around 3250 cm<sup>-1</sup> attributes to the stretching mode of N–H group at the defect sites of the aromatic ring [33]. With respect to CoO, the prominent peak

located at around 440 cm<sup>-1</sup> can be assigned to the stretching vibration of Co–O bond, and the other main band at around 3430 cm<sup>-1</sup> comes from the O–H stretching deformation [34]. After combining CoO with g-C<sub>3</sub>N<sub>4</sub>, all the main characteristic peaks of CoO and g-C<sub>3</sub>N<sub>4</sub> appeared, testifying the coexistence of these two semiconductors in the composite, which is well consistent with the conclusion of XRD.

The SEM image of pure CoO is presented in **Fig. S2**, displaying that the as-prepared CoO consists of large-scale irregular nanoparticles with the diameters of 60–70 nm. The corresponding selective area electron diffraction (SAED) pattern (inset of **Fig. S2**) can further confirm the cubic crystal structure of CoO. **Fig. S3** shows the SEM image of g-C<sub>3</sub>N<sub>4</sub>, exhibiting a wrinkled-layer structure with several stacking layers. Interestingly, when CoO nanoparticles are evenly anchored on the g-C<sub>3</sub>N<sub>4</sub> matrix, the morphology of CoO nanoparticles did not obviously change, but a big difference in their sizes. As shown in **Fig. 2a**, the typical size distributions of CoO embedded in the C<sub>3</sub>N<sub>4</sub> matrix are in the range of 10–20 nm. The smaller particle sizes of CoO are mainly attributed to pre-adsorption of Co<sup>2+</sup> onto the g-C<sub>3</sub>N<sub>4</sub> surface, which restricts the growth of CoO particles [35]. In **Fig. 2b**, a clear lattice spacing of 0.25 nm can be assigned to the (111) crystal plane of CoO [36]. Furthermore, the results from HAADF-STEM image along with the elemental mapping images have demonstrated that the elements of C, N, Co and O are distributed in 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> (**Fig. 2c** and d), which provides a solid evidence for the successful formation of a CoO/g-C<sub>3</sub>N<sub>4</sub> heterostructure.

XPS was in-depth characterized to determine the specific bonding and chemical states of elements in 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> photocatalyst. The full survey spectrum in **Fig. S4** indicates the 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> is composed of C, N, Co, O and In elements. Particular attention should pay to In element, which is from the indium substrate. As shown in **Fig. 3a**, the high-resolution spectrum of Co 2p reveals two typical peaks located at 780.2 and 796.2 eV with another two relatively obvious satellite peaks (786.1 and 802.5 eV), which can be ascribed to the Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> spin-orbit peaks of CoO, respectively [21]. Meanwhile, the O 1s spectrum (**Fig. 3b**) can be subdivided into three peaks at 529.4, 531.2 and 533.1 eV, respectively. The binding energy at 529.4 eV is attributed to the Co–O bond in the CoO phase [37], while the peak at 531.2 eV corresponds to the Co–O–C bond [38], implying that a strong interaction exists between CoO and g-C<sub>3</sub>N<sub>4</sub>. The peak observed at 533.1 eV results from a small amount of physically adsorbed water molecules [39]. In the C 1s spectrum (**Fig. 3c**), three fine peaks located at 284.9, 285.8 and 288.3 eV are in good accordance with C–C coordination, sp<sup>3</sup>-coordinated carbon bonds and N–C=N coordination, respectively [40]. In **Fig. 3d**, the N 1s peak at 398.8 eV ascribes sp<sup>2</sup> hybridized aromatic N bonded to carbon atoms (C=N–C). While the other two peaks at 399.7 and 401.1 eV are attributed to the tertiary nitrogen N-(C)<sub>3</sub> groups and amino groups, respectively [41].

The optical properties of CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> were examined by UV-vis diffuse reflectance spectroscopy and displayed in **Fig. 4a**. As can be seen, pure g-C<sub>3</sub>N<sub>4</sub> (blue line) shows light



**Fig. 1.** (a) XRD patterns and (b) FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub>, CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>.

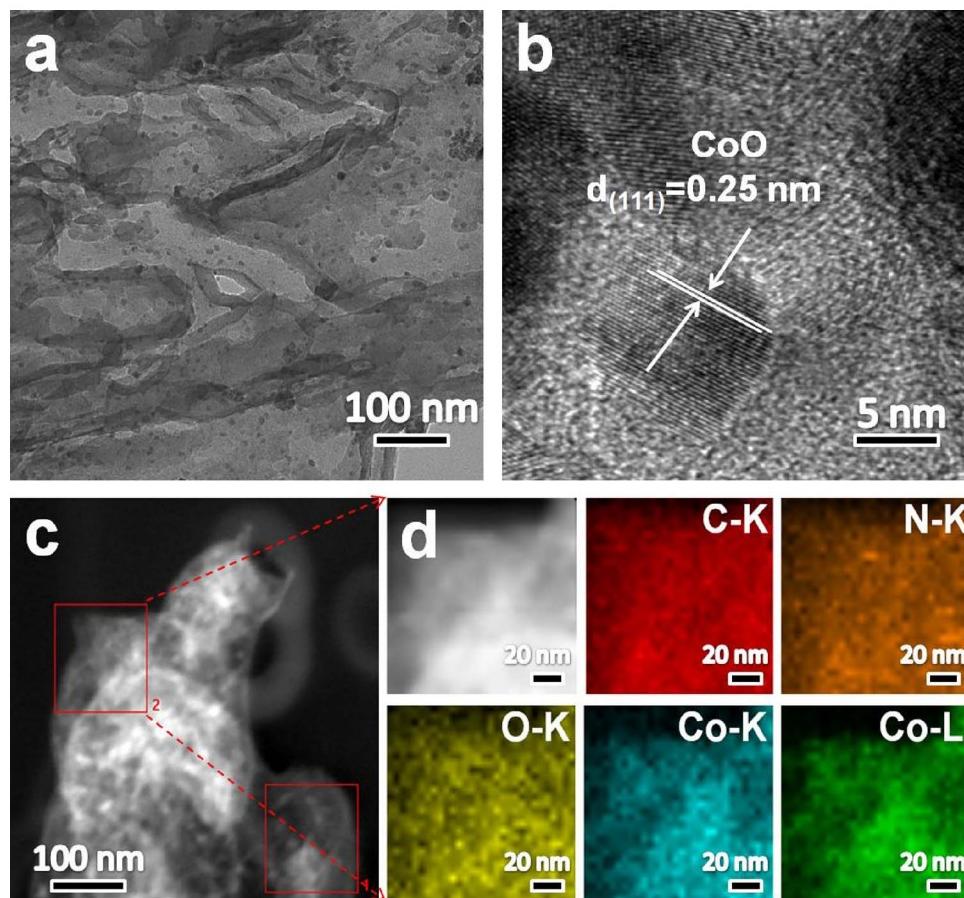


Fig. 2. (a) TEM image, (b) HRTEM image, (c) HAADF-STEM image, and (d) the corresponding elemental mapping images of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>.

absorption below 450 nm and a weaker absorption tail in the visible-light region. The 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> (red line) can absorb more visible light compared with that of g-C<sub>3</sub>N<sub>4</sub>, especially after 420 nm, which can be further verified by the color change of samples from pale

yellow for pure g-C<sub>3</sub>N<sub>4</sub> (blue rectangle box in Fig. 4a) to light grayish for 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> (red rectangle box in Fig. 4a), indicating that CoO to some extent enhances visible-light harvesting. The band gap energies estimated from the Tauc plots of CoO and g-C<sub>3</sub>N<sub>4</sub> are

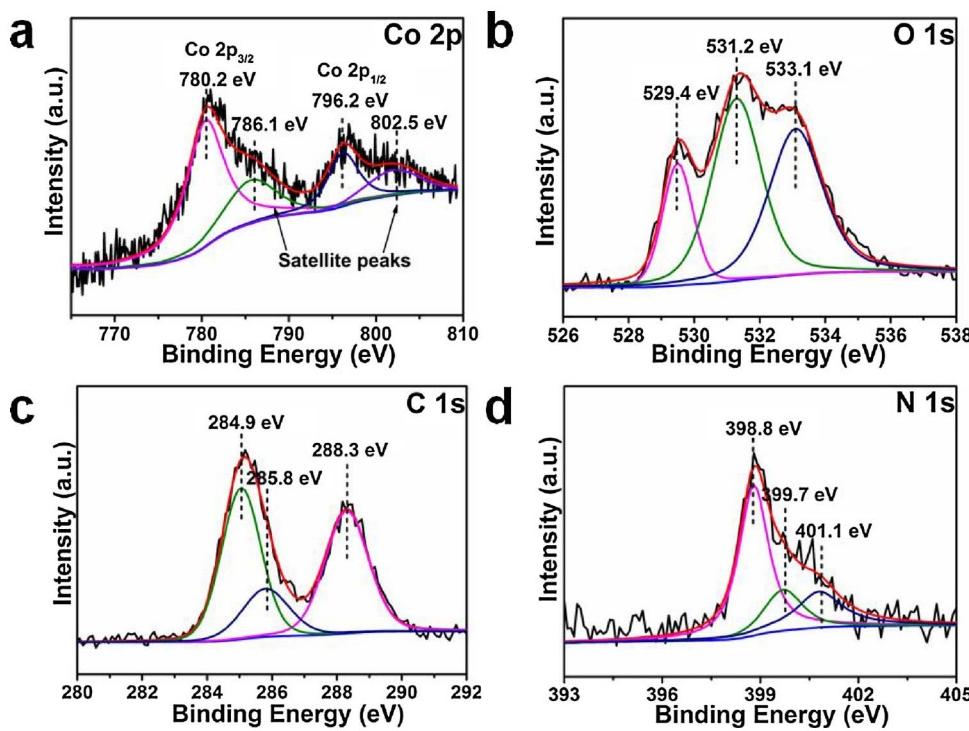


Fig. 3. High-resolution XPS spectra of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> of (a) Co 2p, (b) O 1s, (c) C 1s and (d) N 1s.

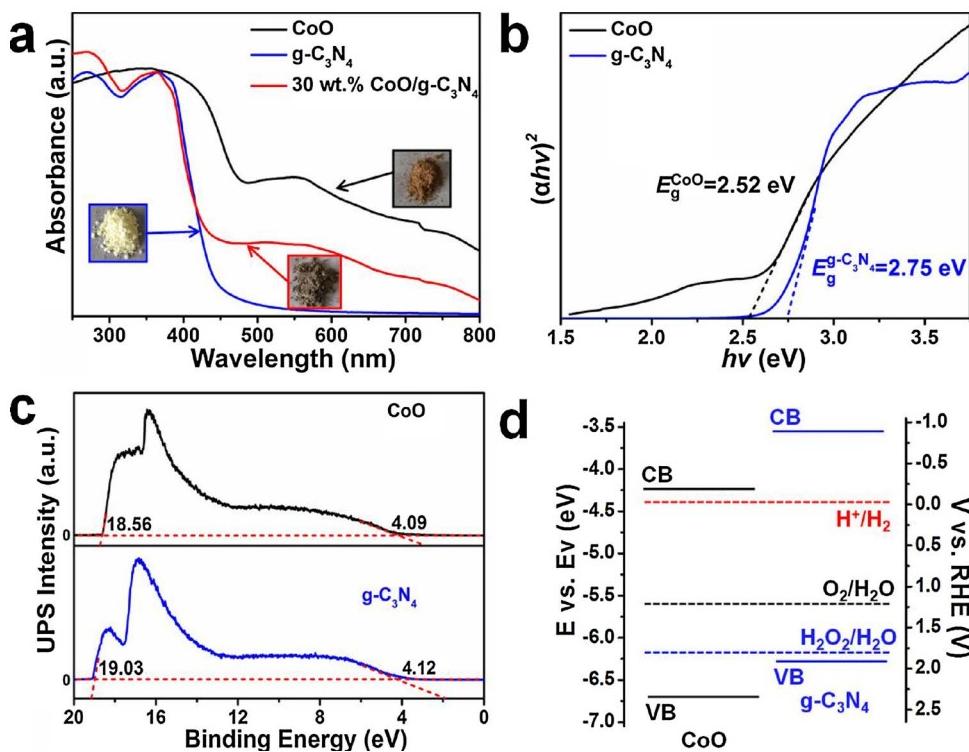


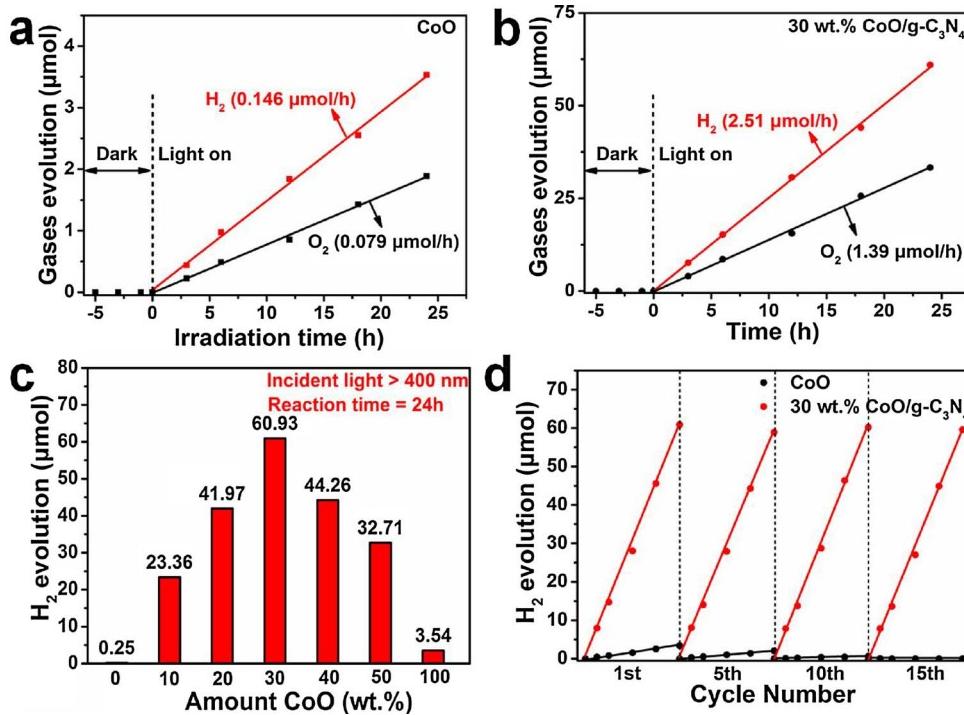
Fig. 4. (a) UV-vis spectra of g-C<sub>3</sub>N<sub>4</sub>, CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>. (b) Tauc plots of  $(\alpha h v)^2$  vs energy ( $h v$ ) for the band gap energy of g-C<sub>3</sub>N<sub>4</sub> and CoO. (c) UPS spectra and (d) the band structure diagrams of CoO and g-C<sub>3</sub>N<sub>4</sub>.

calculated to be 2.52 and 2.75 eV (Fig. 4b), respectively, which are consistent with the previous reported values of CoO and g-C<sub>3</sub>N<sub>4</sub>. Apart from a suitable band gap, the properly matched and positioned both conduction band and valence band levels of two semiconductors are also crucial and essential in designing a heterojunction photocatalyst. Fig. 4c shows the UPS spectra of CoO and g-C<sub>3</sub>N<sub>4</sub> to determine their ionization potentials (equivalent to the  $E_{VB}$ ), which are estimated to be 6.75 eV and 6.31 eV respectively by subtracting the width of the He I UPS spectra (21.22 eV). The  $E_{CB}$  of CoO and g-C<sub>3</sub>N<sub>4</sub> are calculated to be 4.23 and 3.56 eV from  $E_{VB} - E_g$ , which equal to  $-0.21$  and  $-0.88$  V vs. RHE (reversible hydrogen electrode) after converting to electrochemical energy potentials in V, where 0 V vs. RHE equals  $-4.44$  eV vs. vacuum level [30]. Fig. 4d shows the energy level diagrams of CoO and g-C<sub>3</sub>N<sub>4</sub> compared to the potentials for the construction of heterojunction and water splitting. Obviously, the  $E_{VB}$  and  $E_{CB}$  positions of both CoO and g-C<sub>3</sub>N<sub>4</sub> straddle H<sub>2</sub> reduction level, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> oxidation levels for water splitting. Meanwhile, the  $E_{CB}$  and  $E_{VB}$  of g-C<sub>3</sub>N<sub>4</sub> are more negative than those of CoO, and this structure is propitious to the transfer of electrons and holes, indicating that the components of the heterojunction are suitably matched from the band structure. Based on the above analysis, CoO/g-C<sub>3</sub>N<sub>4</sub> as a heterojunction photocatalyst can theoretically realize the overall water splitting into H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>.

In order to evaluate the performance of as-synthesized photocatalysts, the overall water splitting of the samples from pure water under visible light ( $\lambda > 400$  nm) was carried out. The photocatalytic overall water splitting reactions using pristine CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> are shown in Fig. 5a and b. Obviously, it is demonstrated that no H<sub>2</sub> and O<sub>2</sub> can be detected when the system is kept in the dark, but water can be decomposed into H<sub>2</sub> and O<sub>2</sub> with the approximately stoichiometric ratio of around 2:1 over pristine CoO and CoO/g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation. Particularly, H<sub>2</sub> production rate of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> (2.51  $\mu$ mol/h) is nearly seventeen times as high as that of pristine CoO (0.146  $\mu$ mol/h), giving a high AQE of 1.91% at 420 nm. Fig. S5 and Table S1 illustrate the decrease of AQE values with incident wavelengths (420, 450, 535 and 630 nm), which are in agreement with the absorption spectrum of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>, indicating that the reaction is indeed a light-driven redox process. Furthermore, Fig. 5c

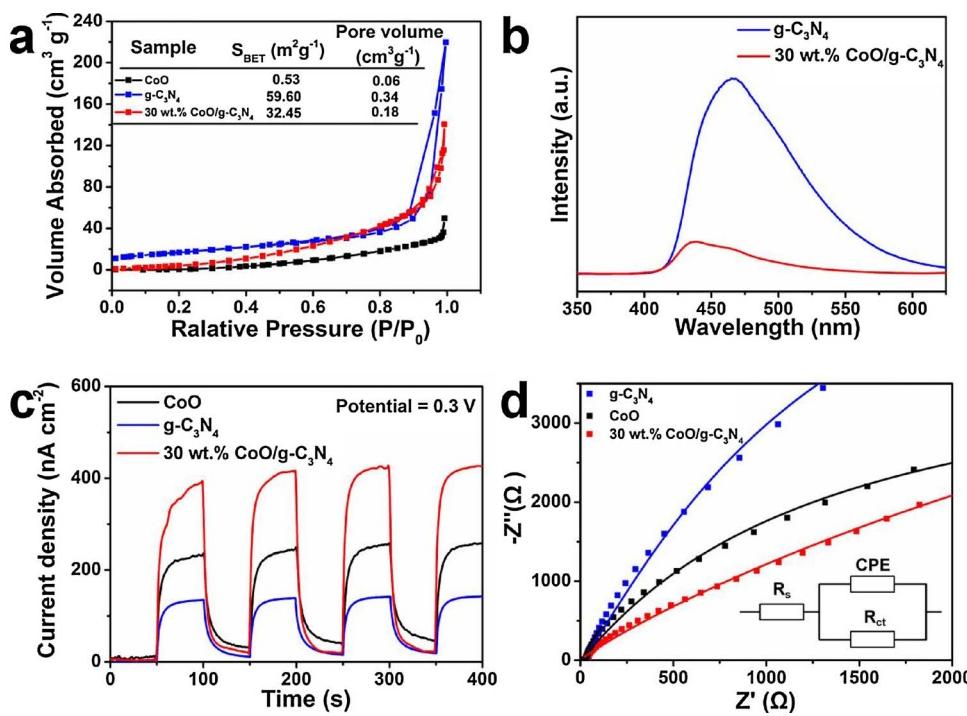
displays the photocatalytic H<sub>2</sub> evolutions from pure water over CoO/g-C<sub>3</sub>N<sub>4</sub> composites with different CoO contents. It is evident that the photocatalytic H<sub>2</sub> production of g-C<sub>3</sub>N<sub>4</sub> can be negligible (0.25  $\mu$ mol within 24 h), and this phenomenon may mainly attribute to the following reasons: (i) fast recombination of electron-hole pairs [42]; (ii) the produced H<sub>2</sub>O<sub>2</sub> during the photocatalytic process leads to fast deactivation of g-C<sub>3</sub>N<sub>4</sub> [29]. However, after combining CoO with g-C<sub>3</sub>N<sub>4</sub>, H<sub>2</sub> production evolution dramatically rises and the optimal content of CoO is obtained by 30 wt.%. Further increasing the content of CoO, H<sub>2</sub> production evolution of CoO/g-C<sub>3</sub>N<sub>4</sub> reveals a somewhat decrease because of the shielding effect of the CoO, also suggesting that the introduction content of CoO does affect the photocatalytic activity in the CoO/g-C<sub>3</sub>N<sub>4</sub> system. Again, the stabilities of CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> were evaluated through recycling experiments under the same condition (Fig. 5d). It displays no apparent deactivation of the 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> photocatalyst after fifteen recycles. Conversely, it is difficult to detect the H<sub>2</sub> production for pure CoO after five successive cycling experiments, demonstrating pure CoO is quite unstable. And this result concurs with our previous report [23]. To further investigate the stability of 30wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>, Fig. S6a and b display that XRD patterns and high-resolution Co 2p XPS of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> before and after reactions, respectively. The intensities and positions of XRD and XPS peaks of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> before and after photocatalysis have no clear change, testifying CoO/g-C<sub>3</sub>N<sub>4</sub> is a stable photocatalyst. Additionally, we also tested the hydrogen production over 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> with different standing times (Fig. S7), showing that although 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> sample is laid aside even for 60 days, it still keeps highly photocatalytic activity. Based on the above analysis, we can safely conclude that the as-prepared CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions indeed exhibit outstanding photocatalytic activity and stability.

For the sake of examining the mechanism for enhanced photocatalytic activity of CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst, multiple techniques were carried out as follows. The BET adsorption isotherms of CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> are displayed in Fig. 6a, where g-C<sub>3</sub>N<sub>4</sub> ( $59.60 \text{ m}^2 \text{ g}^{-1}$ ) shows a much higher specific surface area than 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> ( $32.45 \text{ m}^2 \text{ g}^{-1}$ ) and CoO ( $0.53 \text{ m}^2 \text{ g}^{-1}$ ). This illustrates that the photocatalytic activities of as-prepared samples have



no positive correlation with the specific surface areas, suggesting the specific surface areas of the samples are not the main factor to enhance the photocatalytic performance in this work. Another factor that influences the photocatalytic activity attributes to the efficient separation of electron-hole pairs. It is widely accepted that heterostructure is more beneficial to enhanced photocatalytic activity due to a faster separation efficiency of photo-induced electrons and holes at the interfaces of heterojunctions. PL analysis is commonly applied to study the migration, transfer and recombination of electron-hole pairs generated by the photocatalyst [43]. The PL spectra of g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> with excitation wavelength of 325 nm are shown in Fig. 6b. It can be

**Fig. 5.** H<sub>2</sub>/O<sub>2</sub> evolutions from pure water with (a) CoO and (b) 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> as photocatalysts. (c) H<sub>2</sub> evolutions of CoO/g-C<sub>3</sub>N<sub>4</sub> with different contents of CoO. (d) The stability of photocatalytic water splitting over 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>. The photocatalytic reactions were performed with 50 mg of photocatalyst dispersed in 20 mL of ultrapure water under visible-light irradiation ( $\lambda > 400$  nm).



seen that g-C<sub>3</sub>N<sub>4</sub> exhibits a strong fluorescence emission peak at  $\sim 460$  nm, while the PL intensity of g-C<sub>3</sub>N<sub>4</sub> (still at  $\sim 460$  nm) distinctly decreased after introducing CoO. The lower PL intensity necessarily manifests a slower recombination rate of electron-hole pairs, which indicates a fast interfacial charge transfer between g-C<sub>3</sub>N<sub>4</sub> and CoO in the CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions. Besides, the interfacial charge efficient separation is further verified by the photoelectrochemical technique. Fig. S8 shows the linear sweep voltammetry (LSV) curves of prepared samples which were carried out under xenon lamp irradiation in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Clearly, as-prepared 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> exhibited significantly improved photo-response under light

**Fig. 6.** (a) Nitrogen sorption isotherm and measured parameters (inset) of CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>. (b) The PL spectra of g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> at excitation wavelength of 325 nm. (c) Photocurrent response versus time of as-prepared CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> under xenon lamp irradiation (0.3 V vs. SCE, 100 mW cm<sup>-2</sup>). (d) EIS curves of as-prepared CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub>.

illumination, and the saturation photocurrent reaches  $420 \text{ nA cm}^{-2}$  at  $0.3 \text{ V}$  (vs. SCE), nearly 1.85 and 3 times higher than that of pristine CoO ( $227 \text{ nA cm}^{-2}$ ) and g-C<sub>3</sub>N<sub>4</sub> ( $140 \text{ nA cm}^{-2}$ ) at the same condition, respectively. Furthermore, transient photocurrent responses were conducted in the same electrolytes with interval 50 s light on/off cycle at  $0.3 \text{ V}$  (vs. SCE) shown in Fig. 6c. The as-prepared 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> exhibited excellent photo-stability after 400 s test and achieved higher photocurrent than their sole components, revealing that the existence of heterojunction structure is beneficial to the electron transfer and separation process. EIS measurements of CoO, g-C<sub>3</sub>N<sub>4</sub>, and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> were also conducted as shown in Fig. 6d, offering additional evidence for the enhanced charge separation in the CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction. It can be clearly observed that EIS Nyquist plot of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction has the smallest arc radius in comparison with that of pure g-C<sub>3</sub>N<sub>4</sub> and CoO. The Nyquist plot was also fitted to the equivalent Randle circuit (inset in Fig. 6d) for further analyzing the impedance spectra, where  $R_s$  is the electrolyte solution resistance, CPE is the constant phase element for the electrode and electrolyte interface, and  $R_{ct}$  is the interfacial charge transfer resistance across the electrode/electrolyte [44]. It signifies that 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> exhibited the fastest interfacial charge transfer and the most efficient separation of photo-generated charge carriers.

Moreover, we explored the reasons for the high stability of CoO/g-C<sub>3</sub>N<sub>4</sub>. Sparked by our recent report, experimental results demonstrated that the deactivation of sub-micrometer CoO octahedron photocatalysts resulted from the unintended thermo-induced oxidation during photocatalysis [23]. Similarly, we also further investigated the deactivation reason of CoO nanoparticles in this work. Fig. 7a shows that with increasing the treated temperature, the photocatalytic H<sub>2</sub> production of CoO nanoparticles from pure water rapidly declines. When the treated temperature reached to  $80^\circ\text{C}$ , 24 h photocatalytic H<sub>2</sub> evolution of pure CoO is hardly to be detected. As expected, 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> exhibits excellent heat resistance. It shows that  $70^\circ\text{C}$  treated 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> still continues to generate hydrogen without obvious decrease after three cycles (Fig. 7b). The result partly benefited from the favorable heat conductor of g-C<sub>3</sub>N<sub>4</sub>, which extremely degrades the photo-induced heating of CoO during the photocatalytic reaction.

Meanwhile, from the TEM of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> (Fig. 2a), all the CoO nanoparticles are averagely on the surface of g-C<sub>3</sub>N<sub>4</sub>, thus avoiding the aggregation of CoO, which also protects CoO from the deactivation. Additionally, it should particularly consider another factor is that the existence of H<sub>2</sub>O<sub>2</sub> in water splitting process, which may poison g-C<sub>3</sub>N<sub>4</sub> in this complex photocatalytic system. H<sub>2</sub>O<sub>2</sub> in the reaction solution using CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> as photocatalysts were reflected by UV-vis absorption spectra, where H<sub>2</sub>O<sub>2</sub> were detected in all the photocatalytic systems (Fig. 7c). Unexpectedly, photocatalytic H<sub>2</sub> evolution activity of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> lasts as long as fifteen cycles (Fig. 5d), indicating that CoO may play certain roles in the CoO/g-C<sub>3</sub>N<sub>4</sub>. Thus, we tested the photocatalytic H<sub>2</sub> production of CoO nanoparticles with purposefully adding H<sub>2</sub>O<sub>2</sub> from  $0.01$  to  $0.24 \text{ mol/L}$ , which expectedly indicates no apparent decrease (Fig. S9). The result proves CoO nanoparticles possess excellent H<sub>2</sub>O<sub>2</sub>-resistance poisoning property. Thus, we inferred that when CoO coupled with g-C<sub>3</sub>N<sub>4</sub>, CoO protected g-C<sub>3</sub>N<sub>4</sub> from being poisoned through H<sub>2</sub>O<sub>2</sub> decomposition. In the next experiment, we further characterized the evaluation of O<sub>2</sub> evolution from H<sub>2</sub>O<sub>2</sub> decomposition versus time in the  $10 \text{ mM}$  H<sub>2</sub>O<sub>2</sub> under dark using CoO, 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> as catalysts. It is found that the O<sub>2</sub> evolution rate of 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> is  $0.65 \mu\text{mol}/\text{min}$ , much higher than that of g-C<sub>3</sub>N<sub>4</sub> ( $0.05 \mu\text{mol}/\text{min}$ ), and CoO exhibits the highest O<sub>2</sub> evolution rate ( $0.72 \mu\text{mol}/\text{min}$ ) in Fig. 7d. As a consequence, CoO and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> possess the outstanding ability for the H<sub>2</sub>O<sub>2</sub> decomposition under dark. Based on the above experimental results, we can further conclude that the impressive stability of CoO/g-C<sub>3</sub>N<sub>4</sub> can be attributed to the excellent heat conducting property and large specific surface area of g-C<sub>3</sub>N<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>-resistance property of CoO nanoparticles.

Considering the above analysis and experimental results, a possible photocatalytic mechanism for overall water splitting over CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst was proposed (Fig. 8). And this enhanced and stable photocatalytic activity of CoO/g-C<sub>3</sub>N<sub>4</sub> can be attributed to the complementary advantages between g-C<sub>3</sub>N<sub>4</sub> and CoO in the following reasons: under visible light irradiation, both CoO and g-C<sub>3</sub>N<sub>4</sub> can be excited to generate electrons and holes. Moreover, the excited electrons transfer from the CB of g-C<sub>3</sub>N<sub>4</sub> to that of CoO, while the holes

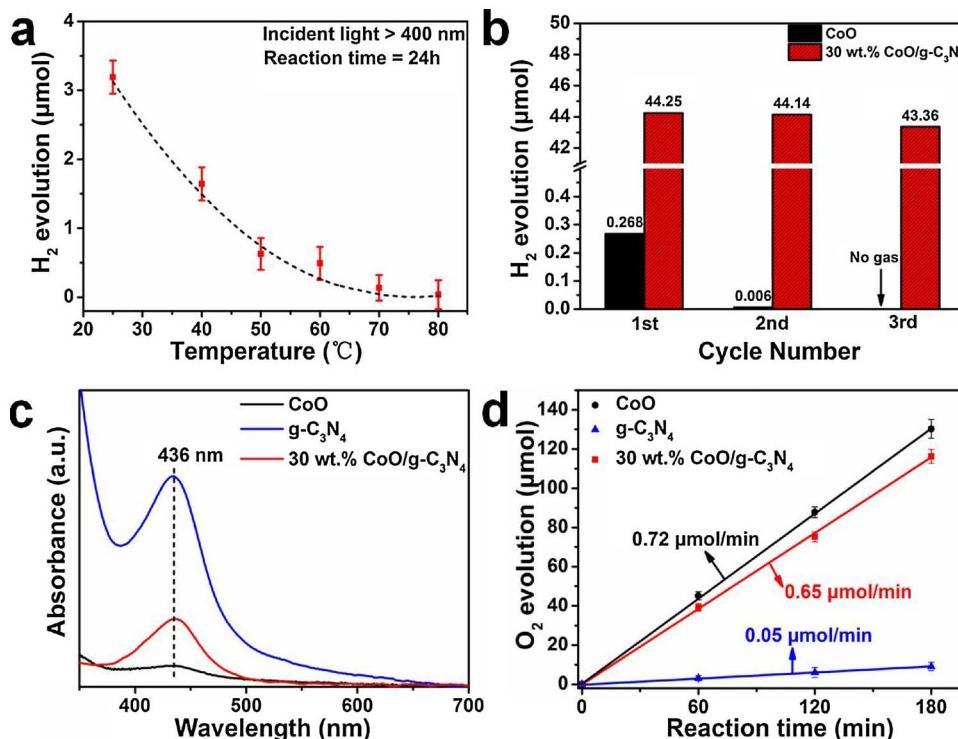
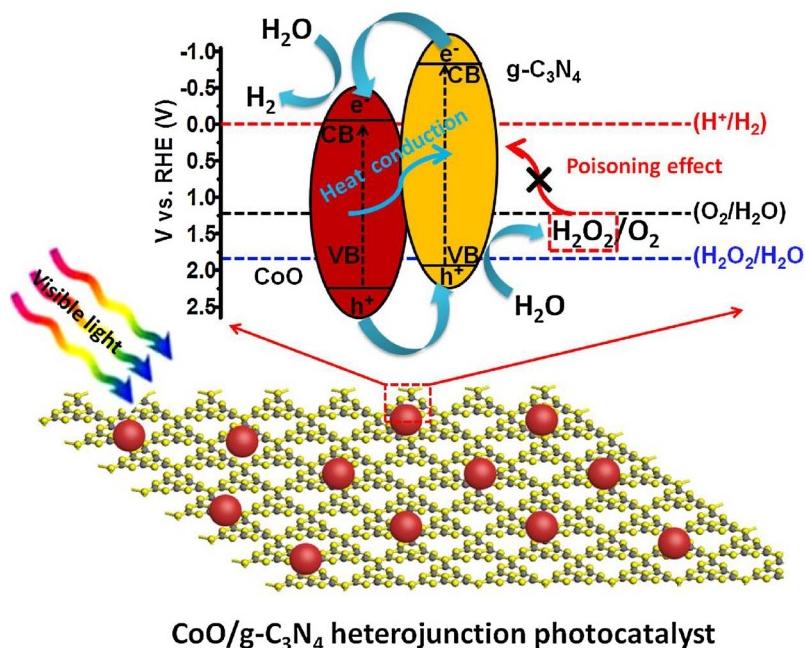


Fig. 7. (a) The variation of photocatalytic H<sub>2</sub> productions (in 24 h) from pure water over CoO by heating at different temperatures. (b) Cycle stability of H<sub>2</sub> production using the  $70^\circ\text{C}$  treated 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> and CoO (each cycle is 24 h). (c) UV-vis absorption spectra of H<sub>2</sub>O<sub>2</sub> in the reaction solution with CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> after 24 h visible light irradiation, respectively. (d) O<sub>2</sub> evolution from H<sub>2</sub>O<sub>2</sub> ( $10 \text{ mM}$ ) decomposition versus time using CoO, g-C<sub>3</sub>N<sub>4</sub> and 30 wt.% CoO/g-C<sub>3</sub>N<sub>4</sub> under dark.



in the VB of CoO transfer to the VB of g-C<sub>3</sub>N<sub>4</sub> due to the well matched band structures of CoO and g-C<sub>3</sub>N<sub>4</sub>. The accumulated electrons on the surface of CoO tend to combine with H<sub>2</sub>O to produce H<sub>2</sub> since the CB (−0.21 V vs. RHE) of CoO is more negative than the reduction potential of H<sup>+</sup> to H<sub>2</sub> (0 V vs. RHE), and holes on the surface of g-C<sub>3</sub>N<sub>4</sub> will react with H<sub>2</sub>O to generate O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, which attributes to the more positive VB of g-C<sub>3</sub>N<sub>4</sub> (1.87 vs. RHE) than O<sub>2</sub>/H<sub>2</sub>O (1.23 V vs. RHE) and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (1.78 V vs. RHE). During the photocatalytic reaction, the unintended produced heating of CoO timely transmits to g-C<sub>3</sub>N<sub>4</sub> owing to the excellent thermal conductivity property of g-C<sub>3</sub>N<sub>4</sub>, simultaneously, outstanding resistance to H<sub>2</sub>O<sub>2</sub> poisoning of CoO immediately decomposes H<sub>2</sub>O<sub>2</sub> to protect g-C<sub>3</sub>N<sub>4</sub> from being poisoned.

#### 4. Conclusion

The CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalysts were fabricated through a facile solvothermal method. In comparison to the single CoO and g-C<sub>3</sub>N<sub>4</sub>, the CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalysts exhibited enhanced photocatalytic activity and long-term stability for overall water splitting under visible light. The optimum photocatalytic activity with approximate stoichiometric ratio of H<sub>2</sub> evolution rate of 2.51 μmol/h and O<sub>2</sub> evolution rate of about 1.39 μmol/h was obtained by the CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunctions with a CoO mass content of 30 wt %. The enhanced photocatalytic activity should be attributed to the effective separation of photogenerated electron-hole pairs in CoO/g-C<sub>3</sub>N<sub>4</sub> heterostructure. And the durable stability is derived from the complementary advantages between CoO and g-C<sub>3</sub>N<sub>4</sub>, in which CoO keeps g-C<sub>3</sub>N<sub>4</sub> from being poisoned by H<sub>2</sub>O<sub>2</sub>, on the contrary, the produced unintended heat from CoO during the photocatalytic reaction is extremely ameliorated after combining with g-C<sub>3</sub>N<sub>4</sub> as a heat conductor. Additionally, g-C<sub>3</sub>N<sub>4</sub> with large specific surface area and flexible 2D structure could effectively prevent CoO aggregation. We anticipate that our idea will provide a new insight of designing heterojunction photocatalysts for photocatalytic hydrogen production to meet the energy demands in the near future.

#### Acknowledgements

This work is supported by the Collaborative Innovation Center of Suzhou Nano Science and Technology, the National Natural Science Foundation of China (51725204, 21771132, 51422207, 51572179,

**Fig. 8.** The possible photocatalytic mechanism for overall water splitting over CoO/g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst.

21471106, 21501126), the Natural Science Foundation of Jiangsu Province (BK20161216) and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.064>.

#### References

- [1] Y.P. Yuan, L.W. Ruan, J. Barber, S.C.J. Loo, C. Xue, Energy Environ. Sci. 7 (2014) 3934–3951.
- [2] A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253–278.
- [3] A. Fujishima, K. Honda, Nature 238 (1972) 37.
- [4] D. Mateo, I. Esteve-Adell, J. Albero, A. Primo, H. García, Appl. Catal. B: Environ. 201 (2017) 582–590.
- [5] Y. Ham, T. Hisatomi, Y. Goto, Y. Moriya, Y. Sakata, A. Yamakata, J. Kubota, K. Domen, J. Mater. Chem. A 4 (2016) 3027–3033.
- [6] J. Xu, C. Pan, T. Takata, K. Domen, Chem. Commun. 51 (2015) 7191–7194.
- [7] F. Vaquero, R.M. Navarro, J.L.G. Fierro, Appl. Catal. B: Environ. 203 (2017) 753–767.
- [8] J. Zhang, Q. Xu, Z. Feng, M. Li, C. Li, Angew Chem. Int. Ed. 47 (2008) 1766–1769.
- [9] E.S. Kim, N. Nishimura, G. Magesh, J.Y. Kim, J.W. Jang, H. Jun, J. Kubota, K. Domen, J.S. Lee, J. Am. Chem. Soc. 135 (2013) 5375–5383.
- [10] A.J. Bard, J. Photochem. 10 (1979) 59–75.
- [11] S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Asai, Z. Li, S.S. Ma, F. Zhang, K. Domen, C. Li, Angew Chem. Int. Ed. 54 (2015) 8498–8501.
- [12] A. Iwase, Y.H. Ng, Y. Ishiguro, A. Kudo, R. Amal, J. Am. Chem. Soc. 133 (2011) 11054–11057.
- [13] K. Maeda, R. Abe, K. Domen, J. Phys. Chem. C 115 (2011) 3057–3064.
- [14] S.R. Lingampalli, U.K. Gautam, C.N.R. Rao, Energy Environ. Sci. 6 (2013) 3589.
- [15] M. Hara, J. Nunoshige, T. Takata, J.N. Kondo, K. Domen, Chem. Commun. (2003) 3000.
- [16] Y. Sasaki, A. Iwase, H. Kato, A. Kudo, J. Catal. 259 (2008) 133–137.
- [17] W.Y. Youngblood, S.H.A. Lee, Y. Kobayashi, E.A. Hernandez-Pagan, P.G. Hoertz, T.A. Moore, A.L. Moore, D. Gust, T.E. Mallouk, J. Am. Chem. Soc. 131 (2009) 926–933.
- [18] J. Jang, H. Kim, U. Joshi, J. Jang, J. Lee, Int. J. Hydrogen Energy 33 (2008) 5975–5980.
- [19] W.-T. Chen, V. Jovic, D. Sun-Waterhouse, H. Idriss, G.I.N. Waterhouse, Int. J. Hydrogen Energy 38 (2013) 15036–15048.
- [20] C. García-Mendoza, S. Oros-Ruiz, A. Hernández-Gordillo, R. López, G. Jácome-Acatitla, H.A. Calderón, R. Gómez, J. Chem. Technol. Biotechnol. 91 (2016) 2198–2204.
- [21] L. Liao, Q. Zhang, Z. Su, Z. Zhao, Y. Wang, Y. Li, X. Lu, D. Wei, G. Feng, Q. Yu, X. Cai, J. Zhao, Z. Ren, H. Fang, F. Robles-Hernandez, S. Baldelli, J. Bao, Nat. Nanotechnol. 9 (2014) 69–73.
- [22] X. Zhan, Z. Wang, F. Wang, Z. Cheng, K. Xu, Q. Wang, M. Safdar, J. He, Appl. Phys. Lett. 105 (2014) 153903.

- [23] W. Shi, F. Guo, H. Wang, S. Guo, H. Li, Y. Zhou, C. Zhu, Y. Liu, H. Huang, B. Mao, Y. Liu, Z. Kang, ACS Appl. Mater. Inter. 9 (2017) 20585–20593.
- [24] P. Niu, L.L. Zhang, G. Liu, H.M. Cheng, Adv. Funct. Mater. 22 (2012) 4763–4770.
- [25] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, Nat. Mater. 8 (2009) 76–80.
- [26] D.T. Morelli, J.P. Heremans, Appl. Phys. Lett. 81 (2002) 5126–5128.
- [27] B. Mortazavi, G. Cuniberti, T. Rabczuk, Comp. Mater. Sci. 99 (2015) 285–289.
- [28] S. Kumar, T. Surendar, B. Kumar, A. Baruah, V. Shanker, J. Phys. Chem. C 117 (2013) 26135–26143.
- [29] J. Liu, N.Y. Liu, H. Li, L.P. Wang, X.Q. Wu, H. Huang, Y. Liu, F. Bao, Y. Lifshitz, S.T. Lee, Z.H. Kang, Nanoscale 8 (2016) 11956–11961.
- [30] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.T. Lee, J. Zhong, Z. Kang, Science 347 (2015) 970–974.
- [31] F. Guo, W. Shi, W. Guan, H. Huang, Y. Liu, Sep. Purif. Technol. 173 (2017) 295–303.
- [32] Q. Qi, Y. Chen, L. Wang, D. Zeng, D.L. Peng, Nanotechnol 27 (2016) 455602.
- [33] W. Shi, F. Guo, J. Chen, G. Che, X. Lin, J. Alloy Compd. 612 (2014) 143–148.
- [34] H. Shi, X. He, J. Phys. Chem. Solids 73 (2012) 646–650.
- [35] P. Suyana, P. Ganguly, B.N. Nair, A.P. Mohamed, K.G.K. Warrier, U.S. Hareesh, Environ. Sci.: Nano 4 (2017) 212–221.
- [36] X. Guan, J. Nai, Y. Zhang, P. Wang, J. Yang, L. Zheng, J. Zhang, L. Guo, Chem. Mater. 26 (2014) 5958–5964.
- [37] Y. Sun, Y. Zhou, C. Zhu, L. Hu, M. Han, A. Wang, H. Huang, Y. Liu, Z. Kang, Nanoscale 9 (2017) 5467–5474.
- [38] Q.M. Yu, J.X. Xu, C.Y. Wan, C.X. Wu, L.H. Guan, J. Mater. Chem. A 3 (2015) 16419–16423.
- [39] S. Xiong, J.S. Chen, X.W. Lou, H.C. Zeng, Adv. Funct. Mater. 22 (2012) 861–871.
- [40] X. Lu, K. Xu, P. Chen, K. Jia, S. Liu, C. Wu, J. Mater. Chem. A 2 (2014) 18924–18928.
- [41] S. Thaweesak, M. Lyu, P. Peerakiatkajohn, T. Butburee, B. Luo, H. Chen, L. Wang, Appl. Catal. B: Environ. 202 (2017) 184–190.
- [42] Q. Han, B. Wang, J. Gao, L.T. Qu, Angew Chem. Int. Ed. 55 (2016) 10849–10853.
- [43] Y.M. He, L.H. Zhang, B.T. Teng, M.H. Fan, Environ. Sci. Technol. 49 (2015) 649–656.
- [44] J. Xu, L.W. Zhang, R. Shi, Y.F. Zhu, J. Mater. Chem. A 1 (2013) 14766–14772.